## Report of Findings for the Lost Creek Fan Nitrate Investigation August-September 2006

Prepared by Laura Alvey
Groundwater Remediation Program/Site Response Section/Remediation Division
Montana Department of Environmental Quality

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## **BACKGROUND**

Elevated nitrate levels in the Lost Creek Fan (LCF) northwest of Kalispell were first noted by the Montana Bureau of Mines and Geology (MBMG) in 1996 as part of a larger investigation of groundwater resources in northwest Montana (LaFave, 2004). The nitrate levels found in 1996 were elevated (above 5 mg/l), but did not exceed the DEQ-7 Montana Numeric Water Quality Standard of 10 mg/l. Later, in 2002, higher levels of nitrate were discovered in groundwater of the LCF. Nitrate-as-nitrogen concentrations (hereafter referred to as "nitrate") in some wells were as high as approximately 40 mg/L, or about 4 times higher than the DEQ-7 Standard. These exceedences were found in residential wells. The Flathead City-County Health Department collected additional samples, and then referred the issue to the Montana Department of Environmental Quality (DEQ) Enforcement Division. The Enforcement Division worked with MBMG to conduct additional groundwater sampling and obtain an understanding of the hydrogeology of the area. The Enforcement Division referred the LCF site to DEQ's Groundwater Remediation Program on May 28, 2004 for further investigation. At this time (February 2007), at least ten domestic wells in the LCF area have levels of nitrate exceeding the DEQ-7 water quality standard of 10 mg/L.

The LCF is generally located in Township 29 North, Range 22 West, Sections 4, 8, 9, and 16 (see Figure 1 in Appendix A). The "fan" can be seen in the contour lines on Figure 1, and is comprised of coarse alluvium (cobbles and boulders) deposited by water from melting glaciers (LaFave, 2004). Lost Creek flows toward the west tip of the fan, is "lost" underground, and is likely a source of groundwater recharge. Many older wells (>15 years) in this area were completed in LCF alluvial deposits at depths from approximately 30-150 feet. This shallow aquifer will be referred to as either the "shallow aquifer" or the "LCF aquifer." Groundwater in the LCF aquifer is thought to flow generally from west to east toward the Stillwater River (see Figure 1) and possibly with surface topography. However, the geology and stratigraphy of the LCF is complex and preferential flow paths may exist. The LCF aquifer overlies a deeper regional aquifer into which most newer wells have been drilled. In this report, the deeper regional aquifer will be referred to as the "deep aquifer" and it will generally be considered to be more than 150 feet deep. Deep groundwater flow in the area of the LCF is also generally to the east and southeast, and eventually toward Flathead Lake (LaFave, 2004).

Currently, the relationship between the shallow and deep aquifer is not well understood. It may be possible that the LCF aquifer and the deep aquifer are hydraulically connected, at least in some areas. If the two aquifers are connected, nitrates could potentially migrate from the shallow to the deep aquifer. It may also be possible that the aquifers were hydraulically distinct in the past, but that the drilling of domestic wells may have provided paths that connect the aquifers. Movement of nitrates from the upper to lower aquifer might also depend, in part, on the differences in hydraulic head (or pressure) in the two aquifers.

Several potential nitrate sources exist or have existed at this site (see Figure 2 in Appendix A). The LCF area was predominantly agricultural until approximately 5-10 years ago, with mint fields, other crops, dairies, and some rangeland interspersed with rural residences. Nitrogen-based fertilizers (both agricultural and residential) are one potential source of nitrates. Dairies and cattle feedlots (with their associated manure piles) are potential nitrate sources, and have operated historically and are still operating in the area. Spreading of septic and dairy waste occurs in the area (spreading of these wastes has been permitted by DEQ's Permitting and Compliance Division), and both of these activities are potential nitrate sources. Residential development has increased dramatically in recent years, and all residences have wells and septic systems. Septic systems are nitrate sources, especially if they were poorly constructed and/or not properly maintained. Residential fertilizer use can also contribute nitrate to groundwater. Poorly constructed and sealed wells can act as conduits for the movement of surface nitrates to the groundwater. Finally, soil disturbance has also been associated with the release of nitrate into the environment.

Nitrate is a biologically active nutrient. It is highly soluble in water and is readily carried by water through soils. In infants less than 6 months old, nitrate can cause a condition called methemoglobanemia which is also known as "blue baby syndrome." Basically, the nitrate is converted to nitrite in the underdeveloped gut of the infant, and the nitrite then prevents the infant's blood from carrying oxygen. Pregnant and nursing women should avoid ingesting nitrate, and nitrate can also pose a health risk to adults with certain chronic health problems. Most of the nitrate ingested by humans comes from vegetables and fruits (lettuce, spinach, celery, greens, melons, etc.), cured meats (bacon, ham, hotdogs, etc.), and dairy products. Nitrates can also enter the body via cigarette smoking and certain medications. When an individual's drinking water source contains elevated nitrate the overall nitrate load to the individual's body increases.

This report discusses the activities and finding of groundwater sampling conducted in August and September 2006. Please note that Figures 1-5 are presented in Appendix A and Tables 1-3 are presented in Appendix B at the end of this document.

## **GOALS**

- **1. Determine plume boundaries and identify additional contaminated wells**. The primary goal of this investigation was to determine the nitrate plume boundaries, both horizontally and vertically. It is possible that some residences are unknowingly using water that exceeds the DEQ-7 standard for nitrate, which can pose health risks. As of November 2005, the MBMG Ground Water Information Center database indicated that there were approximately 50 wells in the study area that are 150 feet deep or less, and 83 wells deeper than 150 feet. It was also anticipated that defining the upgradient boundaries of the elevated nitrate concentrations might assist in determining sources.
- **2. Get current data**. This round of sampling provided a current set of nitrate concentration data. Current data were compared to historical data to assess trends in nitrate concentration.
- **3. Identify sources**. Another goal of this sampling was to gather data, including nitrogen (N)-isotope ratios, potassium (K), chloride (Cl), total phosporus (P), and other parameters, that might provide information regarding nitrogen sources. Five wells were selected for analysis of pharmaceutical compounds. In addition, DEQ and the Montana Department of Agriculture sampled four wells for a suite of pesticides earlier in the summer.

#### **FIELDWORK**

Sample collection was performed according to the August 2006 Sampling and Analysis Plan (SAP) for this investigation. Most samples were collected during the week of August 14, 2006, and three samples were collected on September 21, 2006. As time and access allowed, additional samples were collected from points not previously slated for sampling in the SAP. All sample locations are presented in Table 1 and on Figure 1.

At each sample location, the well was purged (water was run) until water quality parameters stabilized. Water quality parameters were measured with a Horiba Water Quality Checker, and include pH (how acidic or basic the water is), specific conductivity (a measure of the amount of salts dissolved in the water), and temperature. Readings for dissolved oxygen were also collected, but the validity of these readings is suspect because the Horiba meter did not calibrate properly for this parameter. The final readings for each well are presented in Table 2. Sample containers were rinsed three times with sample water prior to sample collection. No sample preservation was required other than putting samples on ice. Well-owners were given sample receipts. No well owners requested split samples.

One well, Schshall, was purged with DEQ's low-flow pump. This well was purged until water quality parameters stabilized. However, it is not certain if the sample was fresh from the formation, or if it was stagnant water that had been sitting in the well. Results from this well should be considered preliminary. DEQ may attempt to resample this well in the future using a different purging method.

No surface water or soil samples were collected in this investigation.

Figure 2 shows some of the possible nitrate sources. When a possible source of nitrate was observed during fieldwork, a Geographic Positioning System (GPS) reading was collected to document the location of the source. Possible sources included a large dairy disposal area on Lost Creek Drive, permitted septage disposal areas, and areas where concentrations and piles of cattle manure was evident. Center pivots and other irrigated/fertilized farmland were not marked with a GPS, but these areas are apparent on aerial photographs (see attached maps). Septic systems were not marked with a GPS, but it can be assumed that for every residence there is a septic system (residences are visible on the attached maps).

At the end of the day or first thing the next morning, samples were delivered to Montana Environmental Laboratories (MEL) in Kalispell for analysis or, for the N-isotope samples, freezing and subsequent shipping. All isotope samples were frozen and shipped to the Marine Biological Laboratory Stable Isotope Laboratory in Woods Hole (MBL), Massachusetts; and two duplicate samples were sent to the isotope laboratory at the University of Waterloo in Waterloo, Ontario, Canada (UOW). Pesticide samples were analyzed at Montana State University in Bozeman. The pharmaceutical samples were analyzed at Columbia Analytical Services (CAS) in Kelso, Washington.

#### **RESULTS**

#### **Data Quality**

Please see Appendix C for a discussion of data quality.

## Well Depths

Samples were collected from 50 total wells. For this report, wells have been divided into two categories: shallow (less than or equal to 150 feet deep) and deep (greater than 150 feet deep). Of the 50 wells, 31 were shallow and 19 were deep.

#### Nitrate Results- Shallow Groundwater in Summer 2006

Figure 3 shows the locations of the shallow nitrate results, and Table 1 lists the nitrate concentrations and other data. Nitrate concentrations in shallow groundwater (wells less than 150 feet deep) ranged from 0.17 (well 1570LCD) to 43.7 mg/l (well 84528). The summer 2006 concentrations are similar to the results from summer 2005. The average nitrate concentration in the shallow groundwater samples was 9.44 mg/l. Of the 31 shallow wells sampled, 11 exceeded the DEQ-7 nitrate standard of 10 mg/l, and 6 wells had "elevated" nitrate concentrations of 5 to 9.9 mg/l. Figure 3 shows the highest nitrate concentrations are located at the northwest corner of the intersection of Farm-to-Market Road and Church Drive in Section 8 (which will be called the "Farm-to-Market Cluster") and north of Church Drive in Section 9 (which will be called the "Church Cluster). The average nitrate concentration in the Farm-to-Market Cluster was 30 mg/l, and 15 mg/l in the Church Cluster.

## Nitrate Results- Deep Groundwater in Summer 2006

Figure 4 shows the locations of the deep nitrate results, and Table 1 lists the nitrate concentrations and other data. In groundwater deeper than 150 feet, nitrate concentrations ranged from 0.03 (1497Church) to 5.98 mg/l (1610Church). The average

"deep" nitrate concentration was 1.3 mg/l. In general, nitrate levels were low (normal) in deep groundwater. The exception is well 1610Church, which had an elevated nitrate level (a concentration greater than 5 mg/l).

#### **Chloride Results**

Table 1 lists chloride results for each sample. Chloride concentrations varied from 0.8 mg/l (in two deep wells) to 71.7 mg/l (in well 148209). In general, chloride concentrations increased with increasing nitrate concentrations (see Figure 7). The average chloride concentration was 13.2 mg/l in shallow wells and 2.54 mg/l in deep wells.

#### **Potassium Results**

See Table 1 for potassium results. All wells but one had potassium ranging from 1 to 3 mg/l. Well 2335WVD was the exception, with potassium at 8 mg/l. The average potassium concentration in the shallow aquifer was 2.6 mg/l, while potassium averaged 1.7 mg/l in the deep aquifer. All samples with nitrate higher than 5 mg/l had potassium concentrations of 2 mg/l or higher. The samples with the lowest potassium concentrations (1 mg/l) were all deep wells with nitrate concentrations less than 3 mg/l (see Figure 10). Figure 10 also shows that most of the wells with potassium at 3 mg/l or higher are shallow wells, while most of the wells with potassium at 2 mg/l or less are deep wells.

#### **Total Phosphorus (P) Results**

Results for total P ranged from "not detected" (less than the laboratory's method detection limit of 0.01 mg/l) to 0.04 mg/l. The highest total P (0.04 mg/l) was from sample 118318, which is the northernmost shallow sample (see Figure 1). Out of the 30 shallow samples analyzed for total P, 22 had non-detectable levels, or about 75%. Out of the 18 deep samples, 7 had non-detectable total P, or about 40%. Of all the samples with nitrate concentrations exceeding 10 mg/l, only one (Lachapshallow) had detectable total P.

#### **Ammonia and Boron Results**

Ammonia (0.02 mg/l) and boron (0.1 mg/l) were both detected in sample Schshall, and were not detected any of the other samples. There are no DEQ-7 groundwater standards for these compounds. Ammonia is an indicator of a low-oxygen environment, and can be present in stagnant water. The Schshall sample was collected from an unused 85-foot deep well using DEQ's low-flow pump. The presence of ammonia may indicate that stagnant water from the well casing was collected, rather than fresh water from the surrounding formation. Boron can be an indicator of septic contamination. The presence of boron may indicate that this well has been impacted by septic leachate, or some other contaminant source that contains boron.

#### Personal Care Products and Pharmaceuticals (PCPPs)

Five wells known to be contaminated with nitrate were selected to provide samples for analysis of PCPPs. These compounds can be indicators of waste water or septic leachate, because these are man-made compounds not found in pristine groundwater, and many are specific to human uses. At least one PCPP was detected in each of the five samples. All

five samples had detections of acetaminophen and progesterone, but these compounds were also detected in the laboratory "blank" and are not listed in the table below. Table 4 (below) lists the sample ID and the PCPPs that were detected.

Table 4: PCPPs in groundwater samples

Sample ID	Compound	Concentration (ng/l = parts per trillion)	Brief description of compound
84527	Gemfibrozil	0.52	Lipid- and cholesterol- modification, decrease risk of heart attack
	Iopromide	3.0	Radioscopic diagnostic aid, increases contrast on medical images
	Sulfamethoxazole	2.2	Antibiotic
84528	Sulfamethoxazole	0.83	See above
137876	Dilantin	2.5	Anti-seizure
	Sulfamethoxazole	40	See above
148209	Iopromide	1.2	See above
	Sulfamethoxazole	34	See above
Lachshallow	Dilantin	2.1	See above
	Sulfamethoxazole	18	See above

There are no DEQ-7 water quality standards for these compounds. Sulfamethoxazole was present in all five samples at concentrations ranging from 0.83 nanograms per liter (ng/l or "parts per trillion") to 40 ng/l. These concentrations are within the range found in a groundwater study of PCPPs in the Helena Valley (Miller and Meek, 2006).

#### **Pesticide Results**

DEQ and the Montana Department of Agriculture selected four wells from which to collect samples for pesticides. Table 5 summarizes the pesticides that were detected and where they were detected. Table 3 (at the end of this document) lists all the pesticides analyzed by the method.

Table 5: Pesticide detection in groundwater samples.

Sample ID	Pesticide	Concentration (ug/l = parts	DEQ-7 Standard	Brief Description of Pesticide
		per million)	(ug/l)	
137876	Bentazon	0.22	200	Registered for use in corn, mint, cereals (wheat), mobile in soils
	Clopyralid	0.038	3,500	a.k.a. Transline <sup>®</sup> , control of broadleaf herbs and noxious weeds (including knapweed and thistles), mobile in soils
84528	Bentazon	0.27	200	See above
84524	None detect	ted	•	
84490	None detect	ted		

## **Nitrogen Isotope Results**

Nitrogen isotope results (listed in Table 1 and shown on Figure 5) ranged from  $\delta^{15}$ N 2.11 to 23.07‰. For the purposes of this investigation,  $\delta^{15}$ N values will be broken down into to "low" ( $\delta^{15}$ N less than 4‰), "medium" ( $\delta^{15}$ N between 4 and 8‰) and "high" ( $\delta^{15}$ N higher than 8‰). Looking at Figure 5, one can see that the all four "low"  $\delta^{15}$ N results (< 4 ‰) are in the Farm-to-Market cluster. Most of the  $\delta^{15}$ N results fall in the "medium" range. A few high  $\delta^{15}$ N values are scattered throughout the LFC. Note that the highest value of 22.07‰ is almost 10 units higher than the next highest result. The 22.07‰ value is from Schshallow, which is the unused well from which the sample was collected with DEQ's low-flow pump. Also, Schshallow had the highest  $\delta^{15}$ N value from Summer 2005 as well as Summer 2006, and there were similar problems properly purging this well in both sampling events.

## **DISCUSSION/CONCLUSIONS**

#### Horizontal nitrate boundaries

One of the goals of this study was to better define the boundaries of the nitrate plume in the LCF area. It appears that there may not be one single nitrate "plume." Rather, there may be multiple sources contributing to elevated nitrates in several areas of the LCF, and perhaps in areas outside of the LCF.

Groundwater in the LCF aquifer is thought to generally flow from west to east, and may flow with surface topography toward the Stillwater River. However, given the rocky subsurface laced with layers of silt and clay, there may be "preferential pathways" or areas where water moves more readily than in other areas, and these pathways may not necessarily flow in concert with the overall flow direction. Preferential pathways could be contributing to inconsistencies in nitrate levels across the fan.

Looking at Figure 3, it appears that the extent of elevated nitrate has been defined on the western tip of the fan and in a northwest to southwest band along the lower edge of the fan. Data from summer 2005 indicated that water in Lost Creek, which may partially recharge LCF groundwater, does not appear to be contributing measurable nitrates to the system. Two shallow wells near Lore Lake, on the north side of the LCF (440SNDLN and 165LLR) were clean, and may define the northern boundary of nitrate in the fan.

A new shallow well (188318) about one mile north of the northern edge of the LCF had nitrate at 8 mg/l, which was not expected, given that this well does not appear to be near any obvious nitrate sources. Also, because the well and development are new, it is unlikely that septic effluent would have had time to impact the well. The nitrate in well 188318 is likely from a different source than the LCF nitrate, given its location and the presence of low-nitrate groundwater between this well and the contaminated LCF wells.

Some inconsistencies in overall nitrate concentration are apparent on Figure 3. First, well 1803Church has nitrate at approximately 2 mg/l, and this well is only about 350 feet south of the "Farm-to-Market" cluster of wells with nitrate concentrations as high as 40 to 50 mg/l. There may be a preferential pathway bringing cleaner water to well

1803Church. Regardless, for reasons currently unknown, well 1803Church has low nitrate concentrations although it is very near three contaminated wells of the same depth as itself.

Another inconsistency is the presence of a shallow well (167042) with very low nitrate levels located across the street from Schshall, a well that had historically high nitrates. Well 167042 is a public water supply well for a dairy, and this well has never shown elevated nitrate levels. Some data (see discussions that follow) indicate that nitrates historically present in Schshall may have been a result of septic contamination. Nitrate plumes from individual septic systems can be relatively limited in size, and that may explain why well 167042 has not seen elevated nitrates.

The downgradient boundary of the elevated nitrates in Section 15 may be defined by well 703038. However, the downgradient boundary has not been defined in the area north of well 703038. Additionally, the cross-gradient boundary has not been defined south of well 2335WVD02 or north of wells 84490 and 84486. More work will need to be done to define areas of elevated nitrates and boundary areas. This task would require expanding the study area, and is limited by where shallow groundwater wells actually exist. DEQ is currently aware of only two additional shallow wells on the LCF which have not been sampled, and these DEQ became aware of only recently.

## Vertical nitrate boundaries: nitrate in the deep aquifer

Nitrate concentrations in the deep aquifer are shown in Figure 4. In general, elevated levels of nitrate were found in the shallow wells and not in deep wells. Nitrate does not appear to be present at levels of concern in groundwater deeper than approximately 150 feet. One exception is well 1610Church (220 feet deep) which had approximately 6 mg/l nitrate, a concentration DEQ considers elevated. The property owner indicated that this well was installed as a replacement for the shallow well on this property, which had been contaminated with nitrate (possibly due to septic effluent contamination). The reason for the elevated nitrates in well 1610Church is not known.

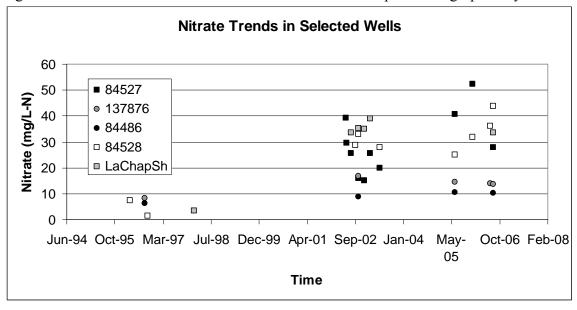
#### Nitrate trends

Table 6 and Figure 6 (below) shows nitrate concentrations over time for selected wells. These wells have the longest and most complete sampling history. There is no clear overall trend. In some wells, nitrate concentrations appear to be fluctuating. These fluctuations do not appear to be consistent between wells (i.e. while nitrate is increasing over time in one well it may be decreasing in another), and do not appear to correlate with seasonal changes in water elevation. There are gaps in the data that make interpretation difficult. Currently, it is unclear if there are seasonal trends in nitrate concentration, or if the fluctuations are due simply to inherent variability in the system. More data points per year would be needed to show seasonal fluctuations and any overall trends. An important item to note is that sometime between 1998 and 2002, nitrate concentrations in several wells (Lachapshallow, 84528, 137876) increased dramatically. Unfortunately, DEQ does not have data for the time period between 1998 and 2002. Also, DEQ does not have data regarding nitrate concentrations in well 84527 prior to May 2002.

Table 6: Nitrate (mg/l) concentrations over time in selected sampling locations.

SampleDate	84527	84572	137876	84486	84490	84516	84528	148210	Lachapshallow
September-96			8.2	6.3	2	5.6	7.5	7.7	
Feb-98									3.54
May-02	39.1								
June-02	29.59							3.55	
July-02	25.62								33.55
September-02							28.64		
October-02	15.86	0.68	16.9	8.7	3	0.9	32.9	5.4	35.35
December-02	15.1	0.75							35.06
February-03	25.63	0.85							38.86
May-03	19.9	0.81				1.42	27.86		
July-05	40.6	0.21	14.48	10.45	6.14	0.99	24.9	8.23	
January-06	52.4						31.9		
July-06			14	_	6.4				
August-06	27.8	1.01	13.6	10.26	5.98	1.8	43.7	8.28	33.5

Figure 6: Nitrate concentrations over time in selected wells presented graphically.



A comparison of nitrate concentrations from all wells from summer 2005 and summer 2006 is presented in Figure 7 (below). There is a strong positive correlation between the two sampling events, which indicates, overall, nitrate concentrations were very similar in summers 2005 and 2006.

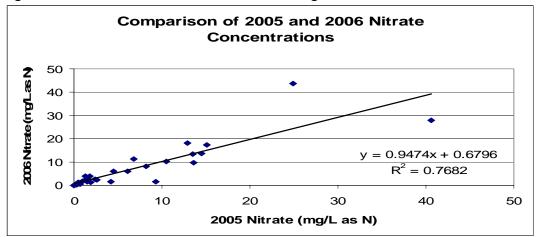


Figure 7: 2006 and 2005 nitrate concentration regression- all wells.

#### **Nitrate and Chloride Correlations**

Samples were analyzed for chloride because chloride, in some cases, can be an indicator of septic effluent contamination (Groundwater Assessment Program, 1999). Figure 8, below, presents a regression analysis of the nitrate and chloride data from all wells. Overall, there is not a strong correlation between nitrate and chloride.

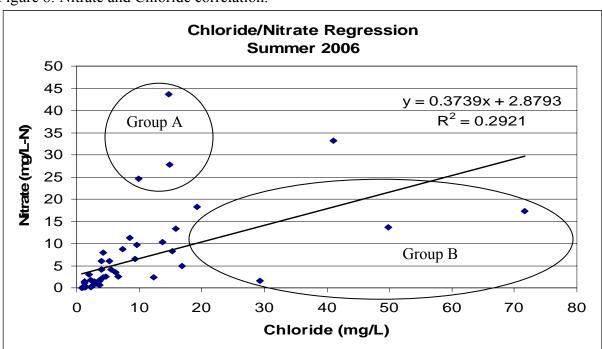


Figure 8: Nitrate and Chloride correlation.

However, it should be noted that, in general, increases in nitrate tend to be accompanied by increases in chloride. The following wells (Group B in Figure 8) had much higher chloride than nitrate concentrations: Schshall, 13876, and 148209. The reason for these variations is unknown, but it is interesting that two of these wells, 137876 and 148209, are in the Church Cluster. Three wells (84528, 84527, and 193337) in Group A of Figure 8 had much higher nitrate than chloride concentrations, and these wells are in the Farmto-Market Cluster near the Section 8 center pivot. At this time DEQ does not have an explanation for these observations, but the different grouping may indicate different nitrate sources.

Both chloride and nitrate are negatively charged monovalent ions, and would therefore be expected to migrate similarly through the soil and groundwater. Chloride is a component of septic waste (from salts in human waste and water softeners), dust suppressants and de-icing solutions applied to roads (magnesium chloride), animal wastes, and some fertilizers (potassium chloride). In some investigations, chloride has been an indicator of septic contamination (Groundwater Assessment Program, 1999). However, local farmers have indicated they use potassium chloride fertilizer for agricultural purposes in the LCF area, so elevated chloride levels in the LCF aquifer cannot necessarily be attributed to septic effluent.

## Nitrate's Relationship to Specific Conductivity

Figure 9 plots Specific Conductivity (SC) versus well depth, and breaks the data down according to nitrate concentration (see Figure 9's legend). SC is a measure of a sample's ability to conduct an electrical current. The saltier a water sample is, the more readily it conducts a current, and the higher the SC will be. In general, Figure 9 shows that as well depth increases, SC decreases. Note that the wells with nitrate concentrations greater than 10 mg/l (the black boxes) have higher SC. This indicates that the source(s) of nitrate may be contributing to an increase in the overall salt concentration of the groundwater.

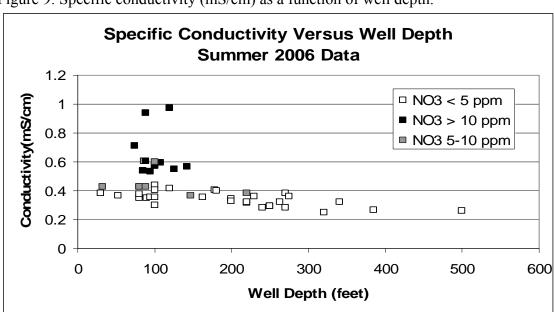


Figure 9: Specific conductivity (mS/cm) as a function of well depth.

## Nitrate's Relationship to pH

Figure 10 (below) is a plot of pH versus well depth, with the data broken down by nitrate concentration. The pH of a sample is a measure of its acidity or basicity, with a pH of 7 being neutral. The pH range for drinking water is typically 6.5 to 8.5. Overall in the LCF samples, as wells get deeper, the pH of the water goes up and becomes slightly basic. Note that all the samples with nitrate greater than 10 mg/l cluster at a pH less than 6.9. This may indicate that the source(s) of nitrate are adding acidity to the groundwater.

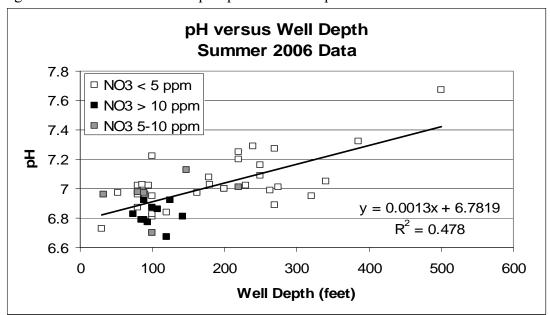


Figure 10: Nitrate's relationship to pH and well depth

#### Nitrate's relationship to Potassium (K)

Figure 11 (below) shows nitrate and potassium concentrations in each sample. All shallow wells have potassium concentrations of 2 mg/l or higher. Only one deep well had a potassium concentration higher than 2 mg/l. In general, deep wells appear to have lower potassium concentrations. Of the wells with nitrate concentrations greater than 10 mg/l, eight had potassium at 3 mg/l and two wells had potassium at 2 mg/l. Well 2335WVD01 had K at 8 mg/l which was more than twice as high as any of the other wells.

Potassium (K) Versus Nitrate 9 8 ☐ shallow wells 7 ■ deep wells Total K (mg/) 6 5 4 3 2 0 0 10 20 30 40 50 Nitrate (mg/L- N)

Figure 11: Potassium concentrations as a function of nitrate concentration.

## **Nitrate's relationship to Total Phosphorus (P)**

Figure 12 shows that high and low concentrations (relative to this investigation) of total P are found in wells of all depths. Figure 12 also shows that, overall, wells with elevated nitrate concentrations have lower P concentrations. This phenomenon is unexplained at this time.

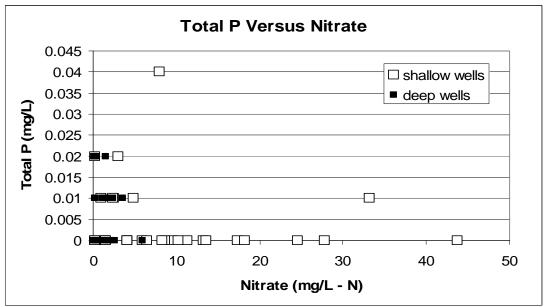


Figure 12: Total phosphorus plotted as a function of nitrate concentration.

## Relationship between Chloride (Cl) and Potassium (K)

Figure 13 shows that, in general, chloride and potassium increase together in concentration. However, Figure 13 also shows that the relationship between chloride and potassium is not strong, as the range of chloride concentrations is large for each unit of potassium.

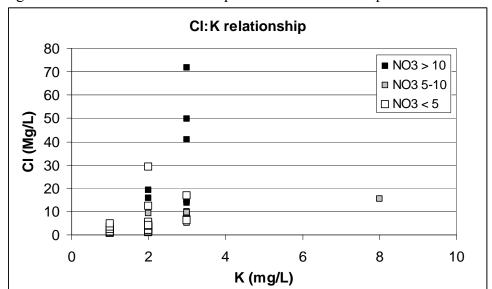


Figure 13: Chloride concentration plotted as a function of potassium.

## **Discussion of Isotope results**

Nitrogen is found in two stable forms (or "isotopes") in nature: "light" nitrogen-14 ( $^{14}$ N) and "heavy" nitrogen-15 ( $^{15}$ N). The two isotopes are found in different ratios in different media. In the laboratory, the ratio of  $^{15}$ N: $^{14}$ N in a sample is compared to the ratio of  $^{15}$ N: $^{14}$ N in the nitrogen (N) gas in air. The isotope data is reported in " $\delta^{15}$ N" values with units of "per mil" (‰), and indicate how much heavy  $^{15}$ N a sample has compared to atmospheric N. Nitrogen in the atmosphere has been assigned a  $\delta^{15}$ N of 0‰. A sample that is enriched in heavy  $^{15}$ N compared to atmospheric N will have a  $\delta^{15}$ N greater than 0‰. A sample that is depleted in  $^{15}$ N compared to atmospheric N will have a  $\delta^{15}$ N less than 0‰ (a negative value). Different sources of N (fertilizer, manure, septic effluent, etc.) can have distinct N isotope ratios, which can allow source identification in some circumstances. Source identification can be complicated or impossible if there is mixing of sources. For reviews of nitrogen isotopes and their use in groundwater investigations, please see Clark and Fritz (1997) and Kendall and Aravena (2000).

In biological systems, enzymes tend to process the light  $^{14}N$  faster than the heavy  $^{15}N$ , which concentrates the  $^{15}N$  in waste materials and drives the  $\delta^{15}N$  value higher than the starting  $\delta^{15}N$  value of the N reservoir. Therefore, one would expect to see higher  $\delta^{15}N$  values in nitrate from septic systems and animal wastes than in atmospheric N. Nitrogen fertilizers synthesized from the N in air, or other sources of synthetic N including explosives, are expected to have  $\delta^{15}N$  values similar to that of air ( $\delta^{15}N$  values close to 0‰). Although some studies have demonstrated that N-isotopes alone can differentiate

between animal versus synthetic N sources (or between sources with known  $\delta^{15}$ N values), there can be some overlap in N isotope values of sources (Kendall and Aravena, 2000; Fogg et. al., 1998; Townsend et. al., 2000; Clark and Fritz, 1997; and Fogg et.al., 1998).

With the exception of the result from the well Schshall ( $\delta^{15}$ N of 22.07‰), nitrogen isotope ratios in this investigation ranged between 2.11 and 12.46‰. In general, septic effluent and animal waste show  $\delta^{15}$ N values of 8‰ or greater, and synthetic nitrogen sources generally have  $\delta^{15}$ N values less than 7‰ (Kendall and Aravena, 2000; Clark and Fritz, 1997). Naturally occurring soil organic matter generally has  $\delta^{15}$ N values between 0 and 4‰ (Fogg et. al., 1998).

In DEQ's LCF report from 2005 (Alvey, 2005), DEQ stated that "Because of the potential for overlap in the  $\delta^{15}N$  values from different suspected sources in the LCF, it will be necessary to collect samples directly from potential sources for N isotope analysis to determine their isotope 'fingerprints.'" Further research of this idea has indicated that this work would be more complicated than originally thought. The  $\delta^{15}N$  value of a source can change in the time between when the N source is at the surface of the soil and when it reaches groundwater. For example, N in a septic tank (mostly ammonia and organic forms of N, also know as "reduced" N) likely has a much lower  $\delta^{15}$ N value than the N as it leaves the septic drainfield (mostly nitrate, or "oxidized" N). The  $\delta^{15}$ N value increases from the tank to the drain field because microbes convert the reduced N to nitrogen gas and nitrate via a process called denitrification. During denitrification, the "light" N moves preferentially into the nitrogen gas, and the "heavy" N concentrates in the nitrate that's left behind to flow to the groundwater. Therefore, taking a  $\delta^{15}$ N "fingerprint" of septic effluent would not be a good indicator of the  $\delta^{15}N$  of the N that's reaching groundwater. The same type of changes in  $\delta^{15}$ N values would be true for other N sources as they move through the environment. In general, it could be predicted that the  $\delta^{15}$ N found in the groundwater would be heavier than that in the surface source. Because of these complicating factors as well as budget limitations, DEQ does not believe that collecting "source" samples for  $\delta^{15}$ N analysis is prudent at this time.

It is possible that more than one source is contributing to the total quantity of nitrate in a given location, and mixing of sources can obscure the meaning of the N isotope results. The  $\delta^{15}$ N values in the range of 6-9‰ appear to be in a "middle ground" where some mixing may be occurring.

Of interest are the results from a nested well pair with both a shallow and a deep well (Lachshallow and 3580Deep). These wells are located within 15 feet of each other. Lachshallow's nitrate concentration was 33.5 mg/l and its  $\delta^{15}$ N was 3.37‰. The nitrate concentration in 3580Deep was 2.42 mg/l and the  $\delta^{15}$ N was 12.29‰. It appears that the nitrates impacting Lachshallow are of a different source than the nitrate that is present in 3580Deep.

Additional discussion follows of N isotope results in their relationship to sources.

## Potential N Sources of the LCF

## Septage Disposal Areas

Land-application of septic waste occurs and has occurred in several areas on the LCF. This activity is permitted by DEQ's Permitting and Compliance Division. Figure 2 shows the locations of currently active septage disposal areas. The shallow wells closest to these areas, including the shallow downgradient well, have normal (low) nitrate concentrations. Therefore, DEQ does not suspect that the septage disposal areas are contributing nitrate to the groundwater in concentrations of concern.

## **Dairy Waste Disposal Area**

Figure 2 shows the location of the Meadow Gold Dairy waste disposal area, just south of Lost Creek Drive. DEQ permits land-application of dairy wastes. Currently, Meadow Gold Dairy is reapplying for a permit to dispose of dairy wastes east of the Hedstrom Dairy. Until a decision is made on the new permit, Meadow Gold Dairy's previous permit conditions are in force. According to the permit on file with DEQ, the dairy waste consists of rinse and wash water from dairy production equipment and whey and rinse water from cheese and buttermilk production. Routine monitoring of two groundwater monitoring wells in the middle of this disposal area from 1991 to 2004 reveal a gradual upward trend in groundwater nitrate concentrations (see Figure 14, below). However, these nitrate concentrations averaged between 1.17 to 7.43 mg/l and have never exceeded the DEQ-7 standard of 10 mg/l. Interestingly, over the same time period, the nitrate concentrations in these monitoring wells have been lower than the concentrations in the nearest contaminated residential wells in the Church Cluster to the southeast of the disposal area.

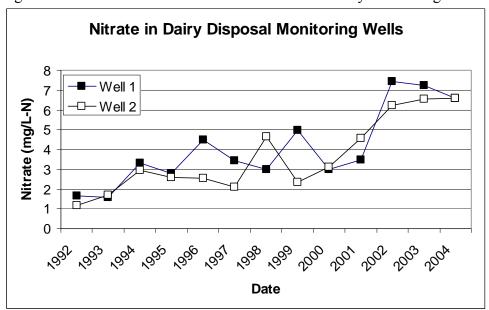


Figure 14: Nitrate concentrations in Meadow Gold Dairy monitoring wells over time.

The dairy disposal monitoring wells have been dry since September, 2004, reflecting a regional lowering of the water table. The dry wells indicate that dairy waste waters are not disposed of in quantities large enough to locally recharge groundwater, although this does not necessarily indicate that contaminants from the disposal area are not reaching groundwater. Meadow Gold monitors the mass of nitrogen and other nutrients being applied to the disposal area as required in their permit, and the annual total mass has never exceeded the permit limits. DEQ reviews monitoring results from the waste itself and groundwater samples to ensure compliance with permit conditions. If dairy wastes were contributing to groundwater N, higher  $\delta^{15}$ N values would be expected than those seen in nearby wells. At this time, DEQ has not ruled out the dairy disposal area as a contributor of nitrates to the groundwater.

#### Cattle Manure

Figure 2 shows the locations of cattle feedlots and other areas where cattle may be concentrated. In general, concentrated cattle areas are located downgradient of existing shallow wells, and downgradient of areas of elevated nitrate concentrations. In most wells located near cattle feedlots, particularly those in the "Church Cluster," the  $\delta^{15}N$  values are too low to point toward a significant contribution of N from manure. If manure were a significant contributor,  $\delta^{15}N$  values greater than 8‰ would be expected.

Well 167042 is located at a dairy, downgradient of the dairy operations and feeding areas, and this well has very low nitrate levels (0.21 mg/l). In this area, it is not expected that cattle manure is impacting groundwater.

One well, 1397Church, is within a feedlot area, has nitrate at 6.44 mg/l, and  $\delta^{15}N$  at 8.11. This data indicates that this well's nitrate may be coming from cattle wastes.

Well 84524 had nitrate at 4.05 mg/l which, although classified as "low" for the purposes of this report, is probably above background nitrate concentrations. This well has a  $\delta^{15}N$  of 11.42‰, which indicates an animal source of nitrate. DEQ understands that a cattle feeding area and associated wastes used to be located just upgradient of this well, although cattle no longer use this area. The nitrate in well 84524 may be a result of cattle manure, although the plume would have been limited in size, given that other wells farther downgradient of well 84524 have very low (background) nitrate concentrations.

Note on Figure 5 that a few other wells have high  $\delta^{15}N$  values, but, based on the information DEQ has at this time, these wells are not located near or downgradient of areas of concentrated animal manure.

#### **Individual Septic Systems**

There is an individual septic system associated with most of the wells on Figure 1. Septic systems can contribute to groundwater contamination either from septic tank failure or from drainfield leachate. Nitrate contamination from septic systems is often accompanied by increases in chloride and other salts, total dissolved solids, metals (including boron), and personal care and pharmaceutical products (PCPPs).

All of the five wells sampled for PCPPs in this investigation had detections of PCPPs. All five of the wells selected for PCPP analysis had elevated nitrate concentrations. The presence of PCPPs in these samples indicates that human-made and human-used compounds have reached groundwater. The PCPP source is very likely from septic effluent because there are no other known sources for these compounds other than septic systems. However, the presence of PCPPs does not necessarily mean that the nitrates in the groundwater are coming from septic systems. An investigation of groundwater in Helena, MT showed that the detections of PCPPs did not correlate with elevated nitrate levels (Miller and Meek, 2006). In the Helena study, PCPPs showed up in almost all wells, even those with low levels of nitrate. This scenario can occur if N from septic systems is retained in the soil or is given off as gas, while certain PCPPs are not degraded or bound in the soil and subsequently leach to groundwater.

Wells contaminated with septic effluent would be expected to have elevated chloride (with chloride concentrations higher than nitrate concentrations),  $\delta^{15}N$  values of 8‰ or higher, and may have detectable boron levels. One well, Schshall, meets all three of these criteria (chloride at 29.3 mg/l,  $\delta^{15}N$  at 23.1‰, and detectable boron), and may be impacted by septic wastes. Although Schshall has not shown high nitrate concentrations in recent sampling events, this well has had elevated nitrate levels in the past, and the current nitrate concentration may be influenced by inadequate purging. It is not expected that inadequate purging would have altered the chloride or boron concentrations. Another factor that points to septic impact in this well is that the well across the street, 167042, has very low nitrate concentrations (0.21 mg/l). Clean well 167042 indicates that the area of nitrate contamination around Schshall is limited in size, as would be expected from a septic plume.

Another well, 2335WVD01, may be impacted by septic effluent (or animal wastes) as this well has  $\delta^{15}$ N of 12.42‰ and a chloride concentration (15.3 mg/l) almost twice as high as its nitrate concentration (8.28 mg/l). Although 2335WVD01 did not have detectable boron, its potassium concentration was 8 mg/l, which is more than twice that of any other well sampled.

Deep well 3580Deep has characteristics of septic contamination, although the nitrate concentration of this well is relatively low. Well 3580Deep has a heavy  $\delta^{15}N$  at 12.29‰, and has higher chloride (4.3 mg/l) than nitrate (2.42 mg/l).

Three other wells have heavy  $\delta^{15}N$  values (84524, 1397Church, and 84486), but the chloride levels in these wells are similar to their nitrate levels, and there are sources other than septic systems near these wells that could be nitrate sources.

Overall, based on  $\delta^{15}N$  and chloride data, there is some evidence that a few wells on the LCF may be impacted by septic leachate, but these are isolated cases. PCPPs were found in all of the five wells sampled for these compounds. Although the presence of PCPPs provides evidence that compounds from septic systems are making their way to groundwater, their presence does not necessarily implicate septic as a nitrate source in large quantity across the LCF. Overall, septic effluent appears to impact individual wells rather than large areas.

#### **Fertilizer**

Fertilizer is used across the LCF for agricultural purposes, as one can see by looking at the green fields in Figure 2. Individual homeowners may use fertilizers for lawns and gardens, and although the quantities for home use are expected to be minor compared to quantities used for agriculture, improper use can cause impact to groundwater. Fertilizer use is much more large-scale, and would be expected to have more consistent and large-scale impacts than the other sources. Fertilizers synthesized from atmospheric N are expected to have  $\delta^{15}N$  values very close to 0‰, and as fertilizer moves through the soil, the  $\delta^{15}N$  value would increase. Other investigations have shown that groundwater impacted by nitrate from fertilizer generally has a  $\delta^{15}N$  range of 0 to 5‰ (Clark and Fritz, 1997). One complicating factor is that the range of  $\delta^{15}N$  of natural soil nitrogen (0-4‰) overlaps with that of synthetic fertilizer. Of the 25 samples analyzed for  $\delta^{15}N$  isotopes, ten had  $\delta^{15}N$  values of 5‰ or less, and six more had values between 5 and 6‰.

A number of samples have characteristics that are consistent with nitrate contamination from fertilizer (have  $\delta^{15}N$  values of 5% or less and are downgradient or located very near areas where fertilizer is used). These wells will be discussed individually or in groups (below):

The shallow wells in the Farm-to-Market Cluster (84527, 84528, and Lachshallow) along with 3745FTM and 193337 generally meet the criteria of fertilizer contamination. Collectively, these wells have the highest nitrate concentrations (average of 27 mg/l) and the lowest  $\delta^{15}N$  values (average  $\delta^{15}N$  of 3.3%) in this investigation. Assuming that groundwater flow is directly to the east, well 84527 does not appear to be directly downgradient of the center pivot to the west of Farm-to-Market Road, but it is possible that groundwater flows to the southeast in this area. A complicating observation is that well 193337, which has elevated nitrate, appears to be directly upgradient of the center pivot. There are no known sources of nitrate upgradient of 193337, and the  $\delta^{15}N$  of 2.8% from this well does not indicate septic or animal waste contamination.

The wells in the Church Cluster (137845, 137876, 14209, and 1481Church) along with 84532 have an average  $\delta^{15}N$  of 5.5%, which is slightly higher than what might be expected if fertilizer was contaminating the water. These wells are approximately one-quarter mile downgradient of areas where fertilizer is used, but are much closer to cross gradient fertilizer use. There are two wells in the Church Cluster that have slightly higher  $\delta^{15}N$  values (137876 and 148209 with  $\delta^{15}N$  values of 6.72 and 5.79%, respectively) than the other wells in this group, and also have the two highest chloride:nitrate ratios of all the samples in this investigation. This may indicate that these two wells have some mixing of sources, and perhaps have some septic contribution.

It is important to note that not all of the wells with low  $\delta^{15}N$  values have elevated nitrate levels. Wells 84572, Pitwell, 1803Church, and 905Clark all have  $\delta^{15}N$  less than 5.5, and nitrate at approximately 4 mg/l or less. Of particular interest is well 84572, which had 1.01 mg/l nitrate and 4.79%  $\delta^{15}N$ . This may indicate that the  $\delta^{15}N$  of the "background" nitrate in the groundwater is naturally close to 5%. Therefore, the "background"  $\delta^{15}N$  of

naturally occurring nitrate in groundwater may overlap in range with that of fertilizer as well as with that of naturally occurring soil N.

Not all of the wells with low  $\delta^{15}N$  and elevated nitrate are downgradient of agricultural fertilizer use. Well 193337 had 24.57 mg/l nitrate, 2.77‰  $\delta^{15}N$ , and is located upgradient of the assumed groundwater flow direction (see Figure 1). Well 188318 has 8.01 mg/l nitrate and 4.3‰  $\delta^{15}N$ , yet there is no apparent fertilizer use upgradient or otherwise near this well. Therefore, it appears that some wells show elevated nitrates consistent with fertilizer contamination, yet, based on land-use, fertilizer use would not be suspected in these areas.

Yet another confounding factor in identifying fertilizer as a nitrate source is that some wells within fertilized fields or immediately downgradient of fertilizer use do not show elevated nitrate concentrations. These wells include Pitwell and 703038. Also, given its close proximity to other contaminated wells, it is puzzling that well 1803Church has low nitrate. One might expect that a large-scale source such as fertilizer would cause a more consistence impact (i.e. more similar nitrate concentrations) across the landscape. In addition, it would be expected that potential impacts from fertilizer would cause increasing nitrate concentration as water moves to the east and intersects more agricultural fields, however, this is not the case (see Figure 3).

It is important to point out that it is not possible to distinguish between residential and agricultural fertilizer based on isotopes. Although smaller quantities of residential fertilizer are used on the LCF compared to quantities used by agriculture, residential use tends to be much less well controlled. Residential fertilizer use often results in overapplication and subsequent leaching. This scenario is especially problematic when a well is located in the vicinity of fertilizer use (i.e. within a lawn or garden). This can be an even bigger problem if the well is not property sealed thereby allowing ready contamination from the ground surface.

Finally, it is important to note again that the  $\delta^{15}N$  range for fertilizers and natural soil nitrogen overlap. DEQ has conferred with an isotope expert at the United Stated Geological Survey (USGS) regarding this issue. The USGS expert indicated that, given the current data, it is not possible to determine whether the nitrate is coming from fertilizer or soil (personal communication, USGS). Soil nitrogen is discussed below. Therefore, at this time, while fertilizer has not been ruled out as a nitrate source for the LCF's groundwater, DEQ had not determined that it is causing the elevated nitrate concentrations in the shallow groundwater.

#### Soil Nitrogen

Nitrogen compounds (nitrate, nitrite, proteins, organic matter, nitrogen gas, etc.) can be present in various forms in soil, including roots and microorganisms, humus and other non-living organic materials, minerals, and soil pore water. When soil is disturbed, the nitrogen can be released from the soil matrix and it then has the potential to migrate to groundwater. Soil disturbance can include tilling, excavation, and erosion. It is not know whether the quantity of nitrogen in LCF soils would be present in quantities large enough to cause the levels of nitrate seen in the wells with the highest nitrate levels. However,

some investigations have found that natural soil nitrogen is capable of causing high levels of nitrate in groundwater (Meehan, 2005), and DEQ has not ruled out soil nitrogen as a possible source of nitrates in groundwater.

## **Overall Conclusions**

Nitrate concentrations remain elevated in the LCF aquifer. There is no obvious trend in nitrate concentrations, but concentrations do not appear to be decreasing. Additional sampling will be needed to determine trends over time. The drought, which has been causing some shallow wells to go dry, may have an effect on the nitrate levels in the LCF aquifer in that there is less recharge and therefore less dilution and flushing of the nitrate than there may be in non-drought years. Alternatively, the drought conditions may be leaving nitrate in the soil profile that would otherwise be moved into the groundwater.

One possible explanation for the increase in nitrate concentrations sometime between 1998 and 2002 may be explained by precipitation patterns. Dry conditions, such as those experienced for a number of years prior to 1999 (El Nino) can cause nitrogen and other nutrients to build up in the soil. The buildup could occur via natural accumulation, or via human-caused sources such as septic systems, fertilizer inputs, cattle manure, etc. In dry years, the nutrients remain in the soil profile rather than migrating groundwater. In 1999, the LCF area saw increased precipitation which could have flushed the nitrate in a pulse to the groundwater and caused the concentration of nitrate to go up. The years following 1999 may have been dry enough that flushing and dilution of the nitrate has not occurred, which may explain, at least in part, why the nitrate levels have not decreased.

At this time, DEQ has not determined the source or sources of elevated nitrate concentrations in various regions of the LCF, although DEQ has ruled-out some sources for certain wells. There are several N sources in the area, and some mixing of nitrate from different sources may be occurring. DEQ has not determined the horizontal extent of elevated nitrate levels in most areas of the LCF because of the lack of monitoring points. In general, it does not appear that the deeper aquifer is experiencing elevated nitrate concentrations.

## Recommendations

- In winter 2007, selected wells should be sampled for nitrate, chloride, and sodium. The sampling emphasis will be on shallow wells and on those deep wells that appear to have elevated nitrate concentrations.
- In spring/summer 2007, all shallow wells that were sampled in 2006 should be resampled, as should any additional sampling points that are identified prior to that sampling event. Selected deep wells should also be sampled. All samples should be sampled for nitrate, chloride, and other parameters as deemed potentially useful. Selected samples may also be analyzed for suites of pesticides/herbicides and/or for a suite of pharmaceutical products.
- DEQ should hire a contractor to construct a potentiometric surface map (groundwater flow direction map) of the shallow aquifer. This map may answer questions about actual groundwater flow directions and preferential flow pathways.
- DEQ should hire a contractor to measure depth-to-groundwater in pairs of deep and shallow wells to determine the hydraulic similarities and differences between the two aquifers. This task would be done in conjunction with the shallow flow map.
- Some studies have shown that analyzing the isotope ratios of the oxygens in nitrate can, in certain circumstances, help to distinguish between soil nitrate and fertilizer nitrate in groundwater. During an upcoming sampling event, selected samples should be analyzed for nitrate-oxygen ratios as well as  $\delta^{15}$ N.
- The shallow wells which could not be sampled due to access issues should be assessed for possible refurbishment and sampling.
- At some point, a plan for sampling soil and other sources should be developed and implemented. However, DEQ does not have the financial resources to conduct this work at this time.
- Ideally, monitoring wells should be installed in critical areas to determine the boundaries of the plume or plumes. The wells would need to be approximately 100 feet deep. Preliminary estimates indicated that the wells could cost approximately \$10,000.00 a piece to install. At this time, DEQ does not have adequate funds to install a monitoring well network at the LCF.

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Appendix A

Figures 1-5

Appendix B

Tables 1-3

				2006	2006	2006	2006	2006	2006	2006
Sample ID	Latitude	Longitude	Well Depth (feet)	Nitrate (mg/L as N)	Chloride (mg/L)	Total Phosphorus	Ammonia (mg/L)	Boron (mg/L)	Potassium (mg/L)	δ15N Isotope value (‰)
PITWELL	48.27738	-114.41092	0	4.05	3.9	< 0.01	< 0.01	< 0.1	2	4.69
2335WVD02	48.2725	-114.38948	30	9.64	9.6	< 0.01	< 0.01	< 0.1	3	6.24
3248FTM	48.27585	-114.42065	30	1.42	2.6	NM	NM	NM	NM	NM
3088CLARK	48.26917	-114.41811	32	4.89	16.9	0.01	< 0.01	< 0.1	3	NM
84572	48.28019	-114.42738	52	1.01	3.2	0.01	< 0.01	< 0.1	2	4.79
LACHSHALLOW	48.28724	-114.41774	74	33.2	41	0.01	< 0.01	< 0.1	3	3.37
LACH08142006 (duplicate of LACHSHALLOW)				33.5	41.2	0.01	<0.01	<0.1	3	3.19
440SNDLN	48.30959	-114.42887	80	2.53	6.6	0.01	< 0.01	< 0.1	3	NM
2111CHURCH	48.28479	-114.43481	80	1.35	3.6	< 0.01	< 0.01	< 0.1	2	NM
1803CHURCH	48.28417	-114.41764	80	1.52	3.7	< 0.01	< 0.01	< 0.1	2	5.12
3745FTM	48.29088	-114.41389	80	8.67	7.4	< 0.01	< 0.01	< 0.1	3	4.92
137875	48.29024	-114.40112	85	13.3	15.8	< 0.01	< 0.01	< 0.1	2	5.46
SCHSHALL	48.29883	-114.4075	86	1.55	29.3	< 0.01	0.02	0.1	2	22.07
84527	48.28482	-114.41759	88	27.8	14.9	< 0.01	< 0.01	< 0.1	3	3.34
84528	48.28649	-114.41892	88	43.7	14.7	< 0.01	< 0.01	< 0.1	3	2.11
84490	48.30387	-114.40891	88	5.98	5.2	< 0.01	< 0.01	< 0.1	3	4.54
1195BRR	48.29292	-114.44231	90	0.21	2.2	< 0.01	< 0.01	< 0.1	2	NM
84532	48.28405	-114.39561	94	11.3	8.5	< 0.01	< 0.01	< 0.1	3	5.13
165LLR	48.31389	-114.41988	95	2.99	2	0.02	< 0.01	< 0.1	2	7.52
703038	48.27858	-114.37698	100	2.38	12.3	0.01	< 0.01	< 0.1	2	NM
2335WVD01	48.27526	-114.38945	100	8.28	15.3	< 0.01	< 0.01	< 0.1	8	12.46
167042	48.29727	-114.40814	100	0.22	1.2	0.02	< 0.01	< 0.1	1	NM
905CLARK	48.29063	-114.39871	100	4.08	4	< 0.01	< 0.01	< 0.1	2	5.48
1570LCD	48.30775	-114.47534	100	0.17	1.2	< 0.01	< 0.01	< 0.1	2	NM
193337	48.29244	-114.4287	100	24.57	9.9	< 0.01	< 0.01	< 0.1	3	2.77
1397CHURCH	48.28404	-114.39383	100	6.44	9.4	< 0.01	< 0.01	< 0.1	2	8.11
137876	48.28876	-114.40002	107	13.6	49.9	< 0.01	< 0.01	< 0.1	3	6.72
84524	48.28438	-114.43943	120	4.05	5.5	< 0.01	< 0.01	< 0.1	2	11.42
844524 (duplicate of 84524)				4.06	5.5	0.01	<0.01	<0.1	2	NM
148209	48.29065	-114.39869	120	17.3	71.7	< 0.01	< 0.01	< 0.1	3	5.79
1481CHURCH	48.28893	-114.39813	125	18.2	19.3	< 0.01	< 0.01	< 0.1	2	4.34

Table 1 continued...

Sample ID	Latitude	Longitude	Well Depth (feet)	Nitrate (mg/L as N)	Chloride (mg/L)	Total Phosphorus	Ammonia (mg/L)	Boron (mg/L)	Potassium (mg/L)	δ15N Isotope value (‰)
84486	48.30218	-114.38783	142	10.26	13.7	< 0.01	< 0.01	< 0.1	3	9.22
844860 (duplicate of 84486)				10.25	13.8	<0.01	<0.01	<0.1	3	8.86
188318	48.32932	-114.42337	147	8.01	4.2	0.04	< 0.01	< 0.1	2	4.3
84516	48.29077	-114.44212	162	1.8	3.7	< 0.01	< 0.01	< 0.1	2	NM
189644	48.2988	-114.42939	178	1.67	2.2	0.01	< 0.01	< 0.1	2	NM
2065WRESERVE	48.24043	-114.39351	180	3.54	6.3	0.01	< 0.01	< 0.1	3	NM
544LLR	48.32111	-114.42947	200	2.57	4.7	< 0.01	< 0.01	< 0.1	1	NM
2950FTM	48.26484	-114.41797	200	1.47	1.3	0.02	< 0.01	< 0.1	2	NM
1497CHURCH	48.28809	-114.40297	220	0.03	0.8	< 0.01	< 0.01	< 0.1	1	NM
1610CHURCH	48.27727	-114.4055	220	5.98	3.9	< 0.01	< 0.01	< 0.1	2	5.72
413LCD	48.30202	-114.40831	220	0.19	1.3	0.02	< 0.01	< 0.1	2	NM
CRMDEEP	48.28437	-114.425	230	1.39	2.8	0.01	< 0.01	< 0.1	2	NM
1555CHURCH	48.28544	-114.40146	240	1.35	3.6	< 0.01	< 0.01	< 0.1	1	NM
121334	48.29906	-114.41373	250	0.49	1.3	NM	NM	NM	NM	NM
SCHDEEP	48.29876	-114.40745	250	0.2	1.1	0.01	< 0.01	< 0.1	1	NM
KLEINDEEP	48.28501	-114.41681	263	0.61	3.7	< 0.01	< 0.01	< 0.1	2	NM
48520	48.29707	-114.418	270	0.24	1.3	0.02	< 0.01	< 0.1	1	NM
84515	48.291	-114.44574	270	0.28	2.4	< 0.01	< 0.01	< 0.1	1	NM
3580DEEP	48.28724	-114.41774	275	2.42	4.3	0.01	< 0.01	< 0.1	2	12.29
15931	48.29021	-114.43187	320	0.04	0.8	NM	NM	NM	NM	NM
2015WVD	48.2674	-114.39217	341	1.06	1.3	0.01	< 0.01	< 0.1	2	NM
139600	48.2961	-114.43707	385	0.15	1.4	0.2	< 0.01	< 0.1	1	NM
725LCD	48.30376	-114.42843	500	0.45	2.5	0.02	< 0.01	< 0.1	2	NM
DEQ-7 Water Quality S	Standard			10	no standard	no standard	no standard	no standard	no standard	not applicab le
Overall Average				6.79	9.63				2.27	6.67
Shallow Average				10.01	13.80				2.61	6.48
Deep Average				1.30	2.54				1.67	9.01
NM = Not Measured										
<b>Bolded</b> values indicate Standard	an exceedance	e of the DEQ-7	Numeric '	Water Quality						

**Table 2: Field-Generated Water Quality Parameters** 

Dissolved Oxygen Sample ID Conductivity (mS/cm) Temperature (°C) (mg/L)\*pΗ **PITWELL** nm nm nm nm 2335WVD02 nm nm nm nm 84572 7.35 0.337 10.8 2.47 440SNDLN 0.431 8.9 -0.35 6.98 2111CHURCH 7.31 0.33 21.4 1.31 1803CHURCH 7.32 0.386 10.6 2.66 137875 7.24 0.507 10 2.15 SCHSHALL 7.53 0.491 10 1.08 84527 7.14 0.625 9.5 2.15 84528 7.18 0.554 12.8 2.66 84490 7.78 0.358 10.6 2.73 1195BRR 7.37 0.327 8.6 2.63 1401CHURCH 7.16 0.506 9.4 1.16 703038 7.28 0.408 11 0.25 2335WVD01 9.9 7.2 0.57 1.72 167042 7.51 0.284 10.5 1.6 137876 7.33 0.524 9.8 1.72 **BR120** 7.31 0.36 11.2 1.47 9.3 1.8 148209 7.18 0.615 1481CHURCH 0.492 9.6 2.35 7.24 84486 7.16 0.542 9.9 1.96 84516 7.33 0.32 10.2 2.62 189644 7.27 0.39 10.2 0.25 **544LLR** 6.86 0.341 9.1 0.18 1497CHURCH 7.07 0.32 9.5 0.03 2.29 1610CHURCH 7.41 0.351 8.9 **CRMDEEP** 7.37 0.356 11.3 2.03 121334 7.4 0.285 11.2 0.285 SCHDEEP 7.44 0.281 12.1 0.36 48520 7.49 0.263 11.2 0.2 84515 7.29 0.359 10.5 1.9 3580DEEP 1.98 7.36 0.345 11.7 15931 7.42 0.241 11.7 0.48 193337 7.56 0.259 11.4 2.12 **Overall Average** 7.31 0.40 10.71 1.51 Shallow Average 7.29 0.45 10.72 1.76 Deep Average 7.33 0.32 10.69 1.13

<sup>\*</sup>The field meter did not calibrate properly for Dissolved Oxygen, so the numbers may not be accurate nm = not measured

The double line divides the "shallow" (150 feet or less) and deep wells (greater than 150 feet)

Table 3: Pesticide results from					DEC 7	IDIT
ANALYTE	137876	84528	84524	84490	DEQ-7 Standard	UNIT
2,4-D	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
2,4-DB	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
2,4-DP	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
3-OH carbofuran	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Acetochlor	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Alachlor	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Aldicarb	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Aldicarb sulfone	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Aldicarb sulfoxide	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Atrazine	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Azinphos Methyl	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Azinphos methyl oxon	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Azoxystrobin	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Bentazon	0.22	0.27	N.D.	N.D.	200	ug/L (ppb)
Bromacil	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Bromuconazole-46	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Bromuconazole-47	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Carbaryl	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Carbofuran	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Chlorsulfuron	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Clopyralid	0.038	N.D.	N.D.	N.D.	3,500	ug/L (ppb)
Cyanazine	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Cyproconazole	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Deethyl atrazine	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Deisopropyl atrazine	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Diazinon	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Dicamba	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Difenoconazole	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Dimethenamid	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Dimethoate	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Disulfoton	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Disulfoton Sulfone	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Disulfoton Sulfoxide	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Diuron	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Epoxyconazole	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Ethion	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Ethoprop	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Fenamiphos	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Fenbuconazole	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Flufenacet OA	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Flumetsulam	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Glutaric Acid	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Halosulfuron methyl	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Hexazinone	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Hydroxy atrazine	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Imazalil	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Imazamethabenz methyl acid metabolite	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Imazamethabenz methyl ester	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Imazamox	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Imazapic	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Imazapyr	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Imazethapyr	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Imidacloprid	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Imine	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)
Isoxazole	N.D.	N.D.	N.D.	N.D.	i ———	ug/L (ppb)

Linuron	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
MCPA	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
MCPP	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Malathion	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Metalaxyl	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Methomyl	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Metolachlor	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Metsulfuron methyl	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Myclobutanil	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
NOA 407854	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
NOA 447204	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Neburon	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Nicosulfuron	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Nitrate as Nitrogen*	14	36	1.6	6.4	10	mg/L (ppm)		
Nitrite as Nitrogen*	N.D.	N.D.	N.D.	N.D.	10	mg/L (ppm)		
Oxazole	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Picloram	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Prometon	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Propachlor	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Propanil	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Propazine	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Propiconazole	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Prosulfuron	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Simazine	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Sulfometuron methyl	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Sulfosulfuron	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Tebuconazole	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Tebuthiuron	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Terbacil	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Terbufos	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Tetraconazole	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Thifensulfuron	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Tralkoxydim	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Tralkoxydim acid	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Triadimefon	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Triadimenol	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Triallate	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Triasulfuron	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Triclopyr	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Trione	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
Triticonazole	N.D.	N.D.	N.D.	N.D.		ug/L (ppb)		
	11.12.	11.12.	11.1.	11.10.		ug E (ppo)		
**************************************								
*Note that nitrate and nitrate are not pesticides. However, the analysis includes these parameters.								
<b>Bolded</b> values indicate that the DEQ-7 Standard is exceeded								
Shaded boxed indicate a detecti				od detect	ion			
limit	on or mo		. 5 0115 111001	401001				
ug/L = "micrograms per liter" =	ppb = "na	arts per bill	ion"					
"5" - IIII O BI WIII POI III OI	77° P					1		

# Appendix C

Discussion of Data Quality and Quality Assurance Quality Control

#### **DATA QUALITY**

## **Inorganic parameters**

Duplicate samples produced very similar or identical results, indicating a high degree of laboratory precision. The relative percent differences (RPDs) for the three nitrate duplicates were 0.9, 0.09, and 0.2 % for samples Lachapshallow, 84486, and 84524, respectively, and the RPDs for the three chloride duplicates were 0.5, 0.7, and 0%, respectively. All duplicate results for total phosphorus, ammonia, boron, and potassium were identical. MEL did not report any problems with analytical methods or data quality. Samples were delivered to the laboratory within holding times and on water-ice.

## **Pesticide samples**

Samples were delivered to the laboratory within holding times and on water-ice. The laboratory did not report any problems with the analytical methods or data quality.

#### Pharmaceutically-active compounds and personal care products

Samples were delivered to the CAS laboratory within holding times. The samples were chilled and shipped with the frozen gel-packs that came with the coolers and bottles. The samples reached the laboratory at approximately 13 degrees Celsius, which is above the generally-required holding temperature of 2-6 degrees Celcius. However, it is expected that any exceedance of holding temperature would bias the results low. Therefore, the detections of analytes in these samples are considered valid for the purpose of determining if the compound was present or not. CAS reported the presence of two compounds (acetaminophen and progesterone) in the internal "blank," which calls into question the validity of these two compounds, which were also detected in the samples. Otherwise, CAS reported no data quality issues that would call into question the validity of the detections of pharmaceutical compounds in the samples.

#### **Nitrogen Isotopes**

Results for nitrogen isotopes ( $\delta^{15}N$ ) are shown in Figure 5 and Table 1. All isotope samples were sent to MLB and UOW frozen. UOW reported no problems with the analytical methods. MLB reported possible problems during sample preparation with a few samples, and these problem samples were reprepared and reanalyzed. There were no problems with the final results. See Table A1 below for a comparison of internal data quality within MLB and between MLB and UOW. The  $\delta^{15}N$  results from summer 2005 and summer 2006 were similar, and this consistency between data sets indicates that the results are very likely accurate and a true measure of the  $\delta^{15}N$  values.

Table C1: Comparison of duplicate samples within and between laboratories

Laboratory (s)	Duplicate Samples	δ <sup>15</sup> N Results for each sample (‰)	Relative Percent Difference	Acceptable? Yes/No
MLB	84486/844860	9.22/8.86	4.2%	Yes
MBL/UOW	84527	3.34/3.49	4.4%	Yes
MBL/UOW	Lachapshallow	3.37/3.19	5.5%	Yes

## Field-Generated Water Quality Data

Table 2 (attached) lists the post-purge water quality parameters collected with the use of a Horiba Water Quality Checker. The meter was calibrated each morning prior to use. Measured parameters included pH, conductivity, temperature, and dissolved oxygen (DO). The meter did not calibrate properly for DO, so these readings are suspect. Also, because the DO readings were not collected "down hole," they may not be representative of actual concentrations of DO in the aquifer.

Overall, the quality of the data gathered during this investigation is acceptable and of sufficiently high quality for the purposes of this study.

